PATENT SPECIFICATION

DRAWINGS ATTACHED

948,085

Date of Application and filing Complete Specification April 7, 1961.

No. 12630/61.

Application made in Germany (No. M45384 IVa/12g) on May 21, 1960.

Complete Specification Published Jan. 29, 1964.

Index at acceptance:—C1 AK5; C5 E(1, 20, B2R)

International Classification:—**C 01 b** (C 07 c, C 10 g)

COMPLETE SPECIFICATION

Method of Carrying Out Exothermic Catalytic Gas Reactions

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, of 14, Reuterweg, Frankfurt-on-the-Main, Germany, a body corporate organised under the Laws of Germany, and STEINKOHLENGAS AKTIENGESELLSCHAFT, of Halterner Strasse, Dorsten, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of converting carbon monoxide in a gas containing the same to carbon dioxide and hydrogen by reaction with steam in the presence of a conversion catalyst.

In exothermic catalytic gas reactions, such as the conversion of carbon monoxide, methane synthesis, or hydrogenation of hydrocarbons, the gas to be treated is generally preheated to the reaction temperature and passed through a reactor in which the gas is contacted with a catalyst. In order to prevent any detrimental increase in temperature from occurring at the catalyst, surplus reaction heat is conducted away from the reactor, either by indirect cooling of the catlyst, or of the gaseous reaction mixture, or by direct cooling by dividing the catalyst into layers or zones and introducing between the layers or zones a cooling gas, for example a gas participating in the reaction, or even water vapour, or by spraying water between these layers or zones. The gaseous reaction mixture flowing into the reactor is heated to reaction temperature for example by means of electric heating, or by indirect heat exchange with the participants in the reaction or parts thereof leaving the reactor.

According to the present invention there is provided a method of converting carbon monoxide in a gas containing the same to carbon dioxide and hydrogen by reaction with steam in the presence of a conversion catalyst, wherein the exothermic conversion reaction is maintained at substantially the desired temperature of between 300 and 400° C. by direct or indirect heat-exchange with a simultaneously occurring endothermic reaction comprising the catalytic cracking or cyclisation of hydrocarbons.

Hydrocarbons which may be evaporated or cracked in the simultaneously occurring endothermic reaction include paraffins, naphthenes or mixtures thereof. The addition of hydrocarbons can be effected in various ways. For example, they can be evaporated into a current of the gaseous reaction mixture to be converted and the mixture of gases and vapours is then heated to the reaction temperature of the exothermic conversion reaction. If the carbon monoxide-containing gaseous mixture contains hydrogen, the hydrocarbons added may contain olefines, alcohols, phenols, sulphur- and nitrogen-compounds which are completely or partly hydrogenated during the reaction with gases containing hydrogen, whereby saturated hydrocarbons, water, hydrogen sulphide and ammonia are produced. In the uppermost catalyst layer hydrogenatable compounds are hydrogenated, the heat produced thereby being utilized for raising the temperature of the catalyst for the exothermic conversion reaction. In this case a catalyst is used which is a catalyst for both the exothermic conversion reaction of the carbon monoxide and the exothermic hydrogenation reaction of the hydrocarbons, and which contains nickel, cobalt, iron, molybdenum, tungsten or a mixture of two or more thereof. The quantity of heat produced during the hydrogenation can be regulated either by the quantity of hydrocarbons added per Nm^3. reaction gas or by the proportion of hydrogenatable compounds in the hydrocarbons or by a combination of both measures.

[*Price 4s. 6d.*]

If the temperature of the exothermic gas reaction is chosen to be sufficiently high, paraffin hydrocarbons or the like can at the same time be split up into smaller molecules.

If the reaction mixture enters the catalyst layer at a temperature of about 300 to 400° C., the conversion of carbon monoxide and steam into carbon dioxide and hydrogen produces so much heat that the following catalyst layers are strongly heated. Hydrocarbons, especially paraffin hydrocarbons, may now be added and completely or partly cracked into smaller molecules, whereby the heat is consumed and consequently the catalyst is cooled. If this heat consumption is not sufficient to cool the catalyst to the desired temperature, further hydrocarbons are either introduced in the form of vapour or sprayed in liquid form, after the first or one of the following catalyst layers. The temperature of the reaction mixture is considerably reduced through the evaporation of the further hydrocarbons, together with the simultaneous cracking and isomerization of the paraffin hydrocarbons as well as the de-hydrogenation of the naphthenes.

During the conversion, a quantity of heat amounting to about 400 kcal. per Nm^3. of carbon monoxide converted into carbon dioxide is produced, which, for example, in the case of the known conversion of water gas containing 40% carbon-monoxide and the usual quantity of steam, leads to an increase in temperature of the reaction mixture by about 150° C. If the temperature of the catalyst is about 350° C., the maximum temperature will then rise to about 500° C

To obtain an extensive carbon monoxide conversion with the smallest possible addition of steam it is necessary, for reasons of equilibrium, to terminate the carbon monoxide conversion at the lowest possible temperature (380 to 400° C.). Therefore, the conversion of carbon monoxide with steam in known processes is usually carried out in two or even three stages, the gas being cooled to about 380° C. after the first stage. The cooling is generally effected by indirect heat exchange or directly by injecting water between the individual stages. This method of heat exchange requires additional expenditure for conduits, and the injection of water is frequently open to the objection that the catalyst becomes encrusted with solids dissolved in the water and its activity is thereby impaired. To avoid this loss of activity of the catalyst and furthermore to simplify the apparatus by using smaller apparatus for the exchange of heat between the reaction products and substances entering the process, hydrocarbons, for example light gasoline or diesel oil or liquid tar fractions, are introduced between the catalyst layers. This results in a gentle cooling of the catalyst which can be adjusted by measuring the quantities of hydrocarbons actually introduced, so that the catalyst is maintained at exactly the temperature which is most favourable for the conversion reaction. The cooling of the catalyst is effected by evaporation of the hydrocarbons and/or by the cracking or dehydrogenation of them, the extent of which is dependent upon the working temperature and the character of the hydrocarbons introduced. Hydrocarbons introduced in a relatively pure state offer the advantage that catalysts which are sensitive to poisoning, e.g. catalysts containing iron oxide and chromium oxide may be used. It is, however, likewise possible to employ hydrocarbons which have not been pre-purified and which contain, for example, sulphur compounds and resinous constituents. In this case, catalysts which are insensitive to poisoning, such as sulphur-resistant catalysts of the cobalt-molybdenum type, are used. Alternatively, when the catalysts are arranged in layers, hydrocarbons, which have not been previously purified, may be introduced in the upper stage or zone for which such an insensitive catalyst is employed, whereas for the other layers or zones which are no longer endangered, an iron oxide-chromium oxide catalyst may be employed.

By a cracking of the additional hydrocarbons introduced into the catalyst, the calorific value of the final gas can also be influenced in the desired manner. For example, if a gas with a high calorific value is required and the initial gas has too low a calorific value, the treatment and especially the cracking of the hydrocarbons introduced is so conducted that large quantities of gaseous hydrocarbons are formed which result in a corresponding increase in calorific value. This manner of working offers the advantage that a subsequent separation of condensible hydrocarbons is not necessary as in the case of the known carburation processes. On the other hand, however, the present method also makes it possible to work in known manner with cracking of the added hydrocarbons into both gaseous and liquid products. Also by controlling the cracking, the method may be carried out without any or with only a slight increase in the calorific value of final gas, and the hydrocarbons introduced may be separated out by condensation after passing through the reactor.

It is furthermore possible to combine with the regulation of temperature by the introduction of hydrocarbons into the catalyst or catalysts, a refinement of these hydrocarbons. If the hydrocarbons are introduced in relatively large quantities and the conversion is carried out at low temperature, a refining of the hydrocarbons then prevails over the cracking.

The present method can be carried out

under normal or superatmospheric pressure with different endothermic gas reactions in combination with the exothermic conversion of gases containing carbon-monoxide. It is possible to carry out cracking, reforming and/or a hydrogenating cracking of hydrocarbons separately or in combination, together or in separate reaction chambers.

Thus, for example, it is possible to carry out a re-formation of gasoline to increase its octane number in an apparatus built like a heat exchanger so that the re-formation takes place in the interior of the pipes and the conversion takes place on the exterior of the pipes.

Where the exothermic and enothermic reactions take place simultaneously in stages running parallel to each other and with heat exchange between the stages, the reactants can flow in co- or counter-current through the catalyst spaces or zones, which may be arranged in layers.

Furthermore, the two reactions can be carried out using different catalysts housed in different compartments or zones of a heat exchanger and the gaseous reactants can be at different pressures within the individual reaction zones in the heat exchanger.

One reaction can be carried out with substances in very pure state using catalysts which are highly sensitive to poisoning, whereas a second reaction can take place in parallel using comparatively impure products and, for example, sulphur-resistant catalysts.

In order to enable to the invention to be more readily understood, reference will now be made to the accompanying drawings, which illustrate diagrammatically and by way of example two embodiments thereof, and in which:—

Fig. 1 illustrates an apparatus for carrying out the carbon monoxide conversion reaction in direct heat exchange with an endothermic reaction.

Fig. 2 illustrates a vertical section through a reactor for carrying out the carbon monoxide conversion reaction using indirect heat exchange between the exothermic conversion reaction and an endothermic reaction.

Referring now to Fig. 1, there is shown apparatus for converting an unpurified initial gas containing carbon monoxide, hydrogen and carbon dioxide. The initial gas comes from a gas generator (not shown) and is mixed with the amount of steam required to effect the conversion reaction (the amount of steam being related to the carbon monoxide content of the gas). The mixture flows at a temperature of 170° C. through a conduit 1 into a heat exchanger 2. On leaving the heat exchanger 2, it is fed at a temperature of about 300° C. through a conduit 3 to a reactor 4 in which the catalyst is accommodated in three layers 5, 6 and 7. In the conduit 3 there is provided an inlet 10 for the introduction of liquid or gaseous hydrocarbons in the initial gas. 9 is an inlet for further hydrocarbons leading to the space between the catalyst layers 6 and 7. Similar inlets can be provided at other points of the reactor. The gaseous reaction product flows out of the reactor at a temperature of about 400° C. and is fed through the heat exchanger 2 and a conduit 8 for further treatment comprising separation of condensable hydrocarbons and removal of carbon dioxide by washing with a liquid absorbent.

The invention will now be further illustrated by the following Examples.

Example 1

A gas containing about 23 Vol.% CO, 40 Vol.% H_2 and 30 Vol.% CO_2 is to be converted to a residual carbon monoxide content of about 5%. The gas, mixed with the requisite amount of steam, enters the reactor at 300° C. and is heated in the first catalyst layer 5 to a temperature of about 350° C., whereupon the conversion reaction commences in the following layer 6 at the desired speed. The increase in temperature is attained by introducing through the inlet 10 400 g. of vapourised gasoline, having a sulphur content of 1%, per Nm^3. of heated gas to be converted before the first catalyst layer 5. The catalyst is, for example, a cobalt-molybdenum catalyst. It effects a hydrogenating refinement of the gasoline and conversion of the initial gas by which at the same time the desired increase in temperature of the gas is attained.

In passing through the second catalyst zone as well as the third zone, for which the same cobalt-molybdenum catalyst or an iron oxide-chromium oxide catalyst may be used, the reaction temperature continues to rise to 450° C. Between the zones 6 and 7 the temperature of the gaseous mixture is reduced to 380° C. by admixing 100 g. per Nm^3. of gas of a gasoline fraction which boils between 40 and 200° C. A gas temperature of 400° C. is then produced at the outlet from the third catalyst layer. This increase in temperature results from the positive conversion heat and the negative heat of cracking.

After cooling the gas in the heat exchanger 2 and separating the condensable compounds and surplus steam in a following cooler, the gas has the following compositions before and after washing to remove the carbon dioxide:—

	Before Washing	After CO_2 Washing
CO_2 - - -	40.7	4.5
C_nH_m - - -	4.8	7.7
CO - - -	5.3	8.6
H_2 - - -	43.0	69.2
CH_4 - - -	5.4	8.7
N_2 - - -	0.8	1.3

Calorific Value 4,600 kcal./Nm^3.

During the cooling of the gas, 320 g./Nm^3. gasoline condensed. It had a boiling range of 32 to 160° C. and its sulphur content amounted to 0.2%.

Example 2.

Referring now to Fig. 2, there is shown a reactor, which is constructed as a tubular heat exchanger. The reactor 11 comprises tubes 12 in which a re-forming catalyst 14 is accommodated, and a conversion catalyst 13 is located in the space between the tubes 12. Gasoline vapours are introduced through a conduit 15, and the re-formed product leaves the reactor through a conduit 16. The gas to be converted enters the reactor at 17 and the converted gas flows out at 18.

The gas containing carbon monoxide and steam which is to be converted is introduced into the reactor at 17 at a temperature of 350° C. It heats up to 450° C. by reaction on the catalyst 13 and during its passage to the outlet from the reactor at 18 the gas is cooled to 400° C. by the heat conducted off to the re-forming reactor. The gasoline vapours enter the reactor at 15 at a temperature of 350° C., and in passing through the re-forming catalyst are first heated to 430° C. and then cooled, so that they leave the re-forming catalyst at 16 at a temperature of 380° C.

The gasoline introduced has a research octane number of 72 which increases to 90 by the reforming. The gas introduced into the conversion catalyst has a carbon monoxide content of 38% which is reduced by the conversion reaction to 4.2%.

WHAT WE CLAIM IS:—

1). A method of converting carbon monoxide in a gas containing the same to carbon dioxide and hydrogen by reaction with steam in the presence of a conversion catalyst, wherein the exothermic conversion reaction is maintained at substantially the desired temperature of between 300 and 400° C. by direct or indirect heat-exchange with a simultaneously occurring endothermic reaction comprising the catalytic cracking or cyclisation of hydrocarbons.

2). A method as claimed in Claim 1, wherein a catalyst for both the exothermic and endothermic reactions is arranged in layers and liquid hydrocarbons to be cracked are sprayed between the layers.

3). A method as claimed in Claim 1 or 2, wherein the catalyst is an iron oxide-chromium oxide catalyst, and/or a sulphur-resistant catalyst, such as a cobalt-molybdenum catalyst, and is a catalyst for both the exothermic and the endothermic reactions.

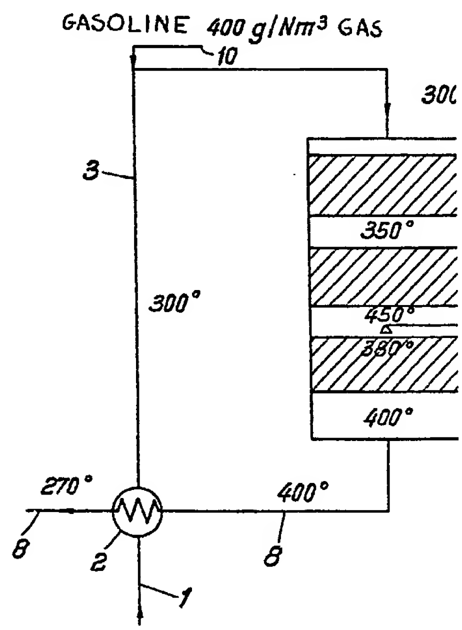
4). A method as claimed in any preceding Claim, wherein hydrogenatable hydrocarbons are added to an initial gas containing carbon monoxide, steam and hydrogen, and wherein the resulting mixture is brought to the required temperature for the conversion reaction by hydrogenating said hydrocarbons.

5). A method of converting a gas containing carbon monoxide and steam at elevated temperature substantially as hereinbefore described with reference to Fig. 1 of the accompanying drawings and the foregoing Example 1, or Fig. 2 of the accompanying drawings and the foregoing Example 2.

THIEMANN, SON & CO.,
Chartered Patent Agents,
Prestige House,
14 to 18, Holborn,
London, E.C.1,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1964.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

Fig. 1



948085 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 1 & 2

Fig. 1

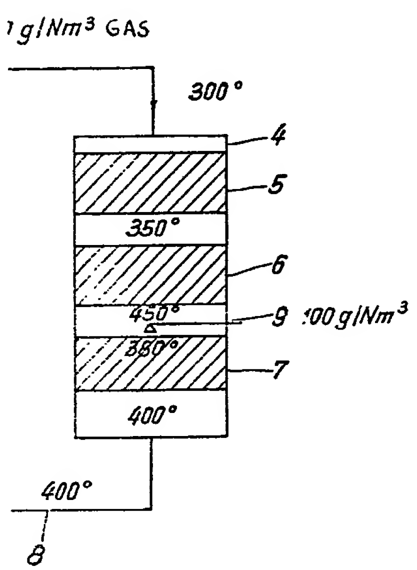


Fig. 2

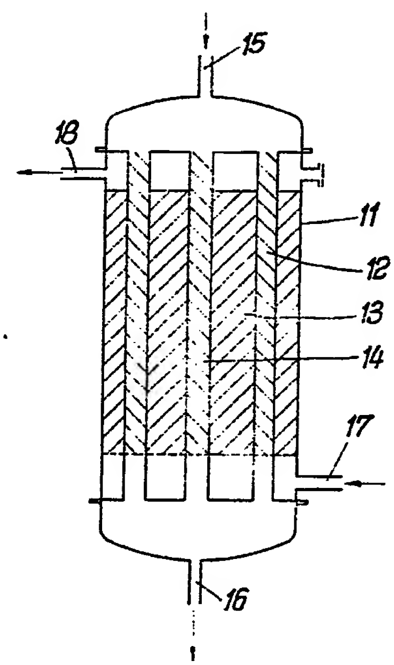


Fig. 1

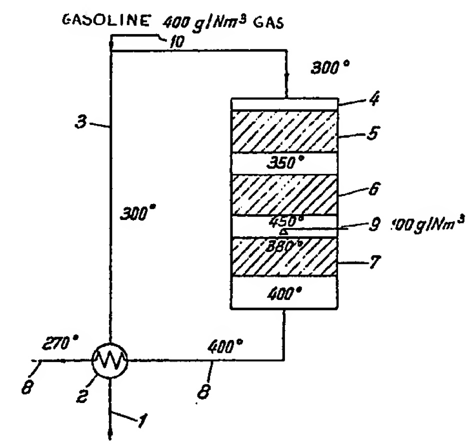
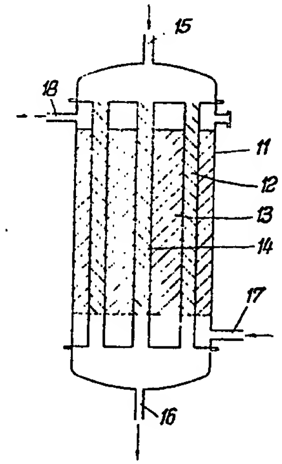

GASOLINE
400 g/Nm³ GAS
10
300°
3
4
5
350°
6
300°
450°
9
100 g/Nm³
380°
7
400°
270°
400°
8
2
8
1

Fig. 2


15
18
11
12
13
14
17
16